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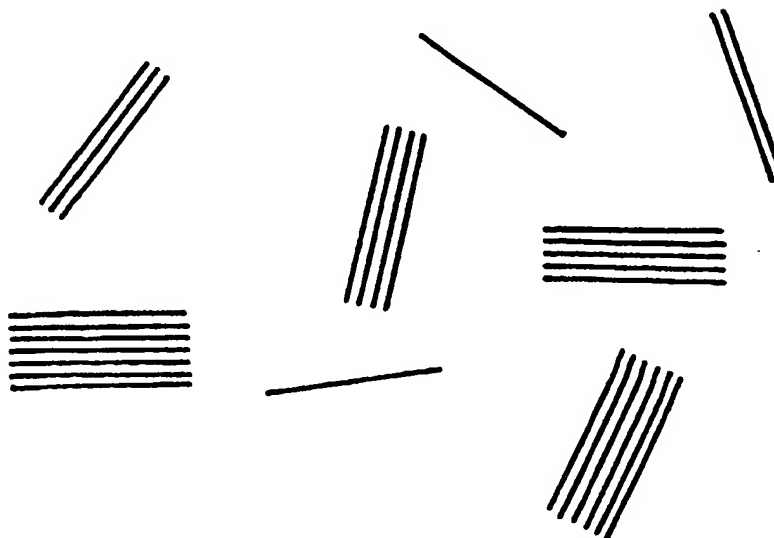
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(54) Title: NANOCOMPOSITE POLYMERS



(57) Abstract: A method for producing a nanocomposite polymer that includes the step of adding an olefin to a metallocene polymerization catalyst treated dispersion of an acid treated cation exchanging layered silicate material in a solvent so that the olefin polymerizes to form the nanocomposite polymer. An exfoliated acid treated cation exchanging layered silicate material dispersed in a polymer matrix, wherein more than about fifty percent of the acid treated cation exchanging layered silicate material is found by electron microscopy to have five or fewer layers. A metallocene polymerization catalyst treated, acid treated cation exchanging layered silicate material.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## NANOCOMPOSITE POLYMERS

## CROSS REFERENCE STATEMENT

This application is under a United States Government Contract Number 70NANB7143028, NIST-ATP Project #570.

## 5 BACKGROUND OF THE INVENTION

The instant invention relates to nanocomposite polymers. European Patent Application publication number EP 0 747 322 A1 describes nanocomposite polymers made by blending quaternary ammonium treated cation exchanging layered silicate materials with a polar group modified polymer. Such nanocomposite polymers exhibit improved  
10 properties such as increased tensile modulus relative to the base polymer. However, the degree of improvement in the properties of such nanocomposite polymers is not as great as desired. It would be an advance in the art of nanocomposite polymers if the degree of improvement were greater. For example, it would be a clear advance in the art if a polypropylene nanocomposite were developed which had a tensile modulus of more than  
15 four hundred thousand pounds per square inch using ten percent or less filler.

## SUMMARY OF THE INVENTION

The instant invention is a solution to the above mentioned problem to a large degree. For example, using the instant invention it is possible to prepare a polypropylene  
20 nanocomposite having a tensile modulus of more than four hundred thousand pounds per square inch using ten percent or less filler.

The instant invention is a method for producing a nanocomposite polymer, comprising the step of adding an olefin to a metallocene polymerization catalyst treated dispersion of an acid treated cation exchanging layered silicate material in a solvent so that  
25 the olefin polymerizes to form the nanocomposite polymer.

In another embodiment, the instant invention is a composition of matter comprising an exfoliated acid treated cation exchanging layered silicate material dispersed in a polymer matrix, wherein more than about fifty percent of the acid treated cation exchanging layered silicate material is found by electron microscopy to have five or fewer layers.

In yet another embodiment, the instant invention is a composition of matter, comprising a metallocene polymerization catalyst treated, acid treated cation exchanging layered silicate material.

## 5 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a drawing reproduction of a photomicrograph of a nanocomposite polymer of the instant invention.

## DETAILED DESCRIPTION OF THE INVENTION

10 The invention is a method for producing a nanocomposite polymer. A nanocomposite polymer is by definition herein a polymer having dispersed therein sufficiently exfoliated cation exchanging layered silicate material. The term "sufficiently exfoliated" means that more than about twenty five percent by weight of the acid treated layered silicate material is found by electron microscopy of the nanocomposite polymer to  
15 have five or fewer layers. Typically, the thickness of a single layer of such material is one to two nanometers while the length and width of such layer can be in the range of, for example, one hundred to one thousand nanometers.

Photomicrographs of nanocomposite polymers typically show a dispersion of multiple layer units of the multi-layered silicate material in the polymer, such as, two, three,  
20 four, five and more than five layer units dispersed in the polymer. It is generally desired to achieve a high degree of exfoliation of the multi-layered silicate material. Ideally the degree of such exfoliation is so extensive that only single layer units are present.

Referring now to Fig. 1, therein is shown a drawing reproduction of an idealized representative photomicrograph of a nanocomposite polymer of the instant invention. Fig. 1  
25 shows two one layer units and one each of a two, three, four, five, six and seven layer unit. The nanocomposite polymer shown in Fig. 1 has about 55 percent five or fewer layer units on a weight percent basis since each of the layers are essentially the same size.

Examples of cation exchanging layered silicate materials include:

- 1) biophilite, kaolinite, dickalite or talc clays,
- 30 2) smectite clays,

- 3) vermiculite clays,
- 4) mica,
- 5) brittle mica,
- 6) Magadiite
- 5 7) Kenyaite,
- 8) Octosilicate,
- 9) Kanemite,
- 10) Makatite, and
- 11) Zeolitic layered materials such as ITQ-2, MCM-22 precursor, exfoliated
- 10 ferrierite and exfoliated mordenite.

Many of the above clay materials exist in nature, and also can be synthesized, generally in higher purity than the native material. Any of the naturally occurring or synthetic cation exchanging layered silicate clay materials may be used in the present invention. Preferred are smectite clays, including montmorillonite, bidelite, saponite and

15 hectorite.

The term "cation exchanging layered silicate material" also includes the "layered fiber" silicate materials such as attapulgite and sepiolite. Layered fiber silicate materials exfoliate to produce multi-fiber units (herein multi-layer units) and most preferably they exfoliate to produce single fiber units (herein single layer units) dispersed in

20 the polymer.

The cation exchanging layered silicate material is acidified by contacting it with a Bronsted acid (such as, hydrochloric acid, sulfuric acid, a carboxylic acid, an amino acid or any material which forms an acidic aqueous dispersion such as acidic metal salts like zinc sulfate) or by contacting it with an acidified amine (such as, an amine hydrochloride

25 such as 4-tetradecyl aniline hydrochloride). Preferably, essentially all of the available cation exchange sites of the layered silicate material are so acidified.

The acidified layered silicate material is dispersed with a solvent (such as, toluene). Most preferably, such dispersion is accomplished by sonication. However, such dispersions can also be made by any suitable technique such as high shear mixing or wet

30 ball milling.

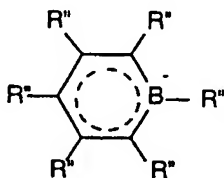
The dispersion may then be contacted with a metallocene polymerization catalyst to produce a metallocene treated sonicated dispersion. Metallocene polymerization catalysts are well known in the art and include derivatives of Group 3, 4, or Lanthanide metals which are in the +2, +3, or +4 formal oxidation state. Preferred compounds include metal  
5 complexes containing from 1 to 3  $\pi$ -bonded anionic or neutral ligand groups, which may be cyclic or non-cyclic delocalized  $\pi$ -bonded anionic ligand groups. Exemplary of such  $\pi$ -bonded anionic ligand groups are conjugated or nonconjugated, cyclic or non-cyclic dienyl groups, allyl groups, boratabenzene groups, and arene groups. By the term " $\pi$ -bonded" is meant that the ligand group is bonded to the transition metal by a sharing or donating of  
10 electrons from a partially delocalized  $\pi$ -bond.

Each atom in the delocalized  $\pi$ -bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, and such  
15 hydrocarbyl- or hydrocarbyl-substituted metalloid radicals further substituted with a Group 15 or 16 hetero atom containing moiety. Included within the term "hydrocarbyl" are C<sub>1-20</sub> straight, branched and cyclic alkyl radicals, C<sub>6-20</sub> aromatic radicals, C<sub>7-20</sub> alkyl-substituted aromatic radicals, and C<sub>7-20</sub> aryl-substituted alkyl radicals. In addition two or more such radicals may together form a fused ring system, including partially or fully hydrogenated  
20 fused ring systems, or they may form a metallocycle with the metal. Suitable hydrocarbyl-substituted organometalloid radicals include mono-, di- and tri-substituted organometalloid radicals of Group 14 elements wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. Examples of suitable hydrocarbyl-substituted organometalloid radicals include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl,  
25 and trimethylgermyl groups. Examples of Group 15 or 16 hetero atom containing moieties include amine, phosphine, ether or thioether moieties or divalent derivatives thereof, e. g., amide, phosphide, ether or thioether groups bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group or to the hydrocarbyl-substituted metalloid containing group.

30 Examples of suitable anionic, delocalized  $\pi$ -bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl,

octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups, and boratabenzene groups, as well as C<sub>1-10</sub> hydrocarbyl-substituted or C<sub>1-10</sub> hydrocarbyl-substituted silyl substituted derivatives thereof. Preferred anionic delocalized  $\pi$ -bonded groups are cyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetramethylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, tetrahydrofluorenyl, octahydrofluorenyl, and tetrahydroindenyl.

The boratabenzenes are anionic ligands which are boron containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in Organometallics, 14,1, 471-480 (1995). Preferred boratabenzenes correspond to the formula:



wherein R'' is selected from the group consisting of hydrocarbyl, silyl, or germyl, said R'' having up to 20 non-hydrogen atoms. In complexes involving divalent derivatives of such delocalized  $\pi$ -bonded groups one atom thereof is bonded by means of a covalent bond or a covalently bonded divalent group to another atom of the complex thereby forming a bridged system.

A suitable class of catalysts are transition metal complexes corresponding to the formula:

$K'_k M Z'_m L_l X_p$ , or a dimer thereof

wherein:

K' is an anionic group containing delocalized  $\pi$ -electrons through which K' is bound to M, said K' group containing up to 50 atoms not counting hydrogen atoms, optionally two K' groups may be joined together forming a bridged structure, and further optionally one K' may be bound to Z';

M is a metal of Group 4 of the Periodic Table of the Elements in the +2, +3 or +4 formal oxidation state;

Z' is an optional, divalent substituent of up to 50 non-hydrogen atoms that together with K forms a metallocycle with M;

5 L is an optional neutral ligand having up to 20 non-hydrogen atoms;

X each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally, two X groups may be covalently bound together forming a divalent dianionic moiety having both valences bound to M, or, optionally 2 X groups may be covalently bound together to form a neutral, conjugated or nonconjugated diene that is  
10 bound to M by means of delocalized  $\pi$ -electrons (whereupon M is in the +2 oxidation state), or further optionally one or more X and one or more L groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto by means of Lewis base functionality;

k is 0, 1 or 2;

15 m is 0 or 1;

l is a number from 0 to 3;

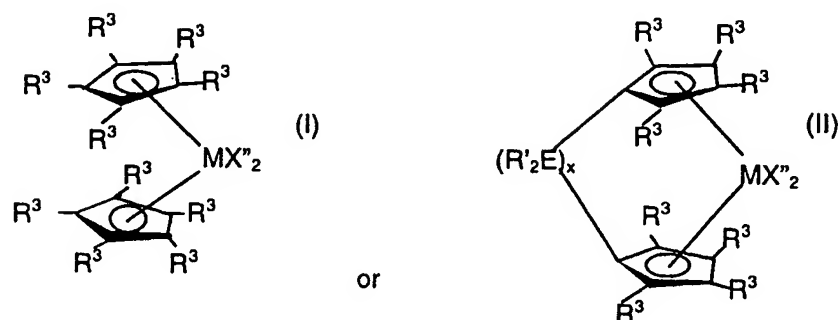
p is an integer from 0 to 3; and

the sum,  $k+m+p$ , is equal to the formal oxidation state of M, except when 2 X groups together form a neutral conjugated or non-conjugated diene that is bound to M via  
20 delocalized  $\pi$ -electrons, in which case the sum  $k+m$  is equal to the formal oxidation state of M.

Preferred complexes include those containing either one or two K' groups. The latter complexes include those containing a bridging group linking the two K' groups. Preferred bridging groups are those corresponding to the formula  $(ER'_2)_x$  wherein E is  
25 silicon, germanium, tin, or carbon, R' independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms, and x is 1 to 8. Preferably, R' independently each occurrence is methyl, ethyl, propyl, benzyl, tert-butyl, phenyl, methoxy, ethoxy or phenoxy.



Examples of the complexes containing two  $K'$  groups are compounds corresponding to the formula:



wherein:

- 5                     $M$  is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the +2 or +4 formal oxidation state;

10                    $R^3$  in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said  $R^3$  having up to 20 non-hydrogen atoms, or adjacent  $R^3$  groups together form a divalent derivative (for example, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system, and

15                    $X''$  independently each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two  $X''$  groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized  $\pi$ -electrons to  $M$ , whereupon  $M$  is in the +2 formal oxidation state, and

$R'$ ,  $E$  and  $x$  are as previously defined.

20                   The foregoing metal complexes are especially suited for the preparation of polymers having stereoregular molecular structure. In such capacity it is preferred that the complex possesses  $C_s$  or  $C_2$  symmetry or possesses a chiral, stereorigid structure. Examples of the first type are compounds possessing different delocalized  $\pi$ -bonded ligand groups, such as one cyclopentadienyl group and one fluorenyl group. Similar systems based on  $Ti(IV)$  or  $Zr(IV)$  were disclosed for preparation of syndiotactic olefin polymers in Ewen, et al., J. Am. Chem. Soc. 110, 6255-6256 (1980). Examples of chiral structures include rac

bis-indenyl complexes. Similar systems based on Ti(IV) or Zr(IV) were disclosed for preparation of isotactic olefin polymers in Wild et al., J. Organomet. Chem., 232, 233-47, (1982).

Exemplary bridged ligands containing two  $\pi$ -bonded groups are:

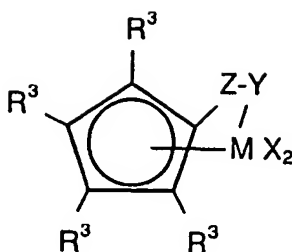
5 dimethylbis(cyclopentadienyl)silane, dimethylbis(tetramethylcyclopentadienyl)silane, dimethylbis(2-ethylcyclopentadien-1-yl)silane, dimethylbis(2-*t*-butylcyclopentadien-1-yl)silane, 2,2-bis(tetramethylcyclopentadienyl)propane, dimethylbis(inden-1-yl)silane, dimethylbis(tetrahydroinden-1-yl)silane, dimethylbis(fluoren-1-yl)silane, dimethylbis(tetrahydrofluoren-1-yl)silane, dimethylbis(2-methyl-4-phenylinden-1-yl)silane, 10 dimethylbis(2-methylinden-1-yl)silane, dimethyl(cyclopentadienyl)(fluoren-1-yl)silane, dimethyl(cyclopentadienyl)(octahydrofluoren-1-yl)silane, dimethyl(cyclopentadienyl)(tetrahydrofluoren-1-yl)silane, (1, 1, 2, 2-tetramethyl)-1, 2-bis(cyclopentadienyl)disilane, (1, 2-bis(cyclopentadienyl)ethane, and dimethyl(cyclopentadienyl)-1-(fluoren-1-yl)methane.

15 Preferred X'' groups are selected from hydride, hydrocarbyl, silyl, germyl, halohydrocarbyl, halosilyl, silylhydrocarbyl and aminohydrocarbyl groups, or two X'' groups together form a divalent derivative of a conjugated diene or else together they form a neutral,  $\pi$ -bonded, conjugated diene. Most preferred X'' groups are C<sub>1-20</sub> hydrocarbyl groups.

20 A further class of metal complexes utilized in the present invention corresponds to the preceding formula  $K'_k M Z'_m L_n X_p$ , or a dimer thereof, wherein Z' is a divalent substituent of up to 50 non-hydrogen atoms that together with K' forms a metallocycle with M.

25 Preferred divalent Z' substituents include groups containing up to 30 non-hydrogen atoms comprising at least one atom that is oxygen, sulfur, boron or a member of Group 14 of the Periodic Table of the Elements directly attached to K', and a different atom, selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur that is covalently bonded to M.

30 A preferred class of such Group 4 metal coordination complexes used according to the present invention corresponds to the formula:



wherein:

M is titanium or zirconium, preferably titanium in the +2, +3, or +4 formal oxidation state;

5  $R^3$  in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said  $R^3$  having up to 20 non-hydrogen atoms, or adjacent  $R^3$  groups together form a divalent derivative (for example, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

10 each X is a halo, hydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 non-hydrogen atoms, or two X groups together form a neutral  $C_{5-30}$  conjugated diene or a divalent derivative thereof;

Y is -O-, -S-, -NR'-, -PR'-; and

Z is  $SiR'_2$ ,  $CR'_2$ ,  $SiR'_2SiR'_2$ ,  $CR'_2CR'_2$ ,  $CR'=CR'$ ,  $CR'_2SiR'_2$ , or  $GeR'_2$ ,

15 wherein  $R'$  is as previously defined.

Illustrative Group 4 metal complexes that may be employed in the practice of the present invention include:

cyclopentadienyltitaniumtrimethyl,

cyclopentadienyltitaniumtriethyl,

20 cyclopentadienyltitaniumtriisopropyl,

cyclopentadienyltitaniumtriphenyl,

cyclopentadienyltitaniumtribenzyl,

cyclopentadienyltitanium-2,4-dimethylpentadienyl,

cyclopentadienyltitanium-2,4-dimethylpentadienyl•triethylphosphine,

- cyclopentadienyltitanium-2,4-dimethylpentadienyl•trimethylphosphine,  
 cyclopentadienyltitaniumdimethylmethoxide, cyclopentadienyltitaniumdimethylchloride,  
 pentamethylcyclopentadienyltitaniumtrimethyl,  
 indenyltitaniumtrimethyl,  
 5 indenyltitaniumtriethyl,  
 indenyltitaniumtripropyl,  
 indenyltitaniumtriphenyl,  
 tetrahydroindenyltitaniumtribenzyl,  
 pentamethylcyclopentadienyltitaniumtriisopropyl,  
 10 pentamethylcyclopentadienyltitaniumtribenzyl,  
 pentamethylcyclopentadienyltitaniumdimethylmethoxide,  
 pentamethylcyclopentadienyltitaniumdimethylchloride,  
 bis( $\eta^5$ -2,4-dimethylpentadienyl)titanium,  
 bis( $\eta^5$ -2,4-dimethylpentadienyl)titanium•trimethylphosphine,  
 15 bis( $\eta^5$ -2,4-dimethylpentadienyl)titanium•triethylphosphine,  
 octahydrofluorenyltitaniumtrimethyl,  
 tetrahydroindenyltitaniumtrimethyl,  
 tetrahydrofluorenyltitaniumtrimethyl,  
 (tert-butylamido)(1,1-dimethyl-2,3,4,9,10- $\eta$ -1,4,5,6,7,8-  
 20 hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,  
 (tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10- $\eta$ -1,4,5,6,7,8-  
 hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl) dimethylsilanetitanium dibenzyl,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium dimethyl,  
 25 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dimethyl,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -indenyl)dimethylsilanetitanium dimethyl,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilane titanium (III)  
 2-(dimethylamino)benzyl;  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (III) allyl,  
 30 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (III)  
 2,4-dimethylpentadienyl,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (II)

- 1,4-diphenyl-1,3-butadiene,  
(tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (II)  
1,3-pentadiene,  
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-  
5 butadiene,  
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,  
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-  
butadiene,  
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) isoprene,  
10 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,  
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)  
2,3-dimethyl-1,3-butadiene,  
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)  
isoprene  
15 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dimethyl  
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dibenzyl  
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,  
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,  
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-  
20 1,3-butadiene,  
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,  
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dimethyl,  
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dibenzyl,  
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II)  
25 1,4-diphenyl-1,3-butadiene,  
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,  
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,  
(tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (IV)  
1,3-butadiene,  
30 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (IV)  
2,3-dimethyl-1,3-butadiene,  
(tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (IV)

- isoprene,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethyl-silanetitanium (II)  
 1,4-dibenzyl-1,3-butadiene,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (II)  
 5 2,4-hexadiene,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethyl-silanetitanium (II)  
 3-methyl-1,3-pentadiene,  
 (tert-butylamido)(2,4-dimethylpentadien-3-yl)dimethylsilanetitaniumdimethyl,  
 (tert-butylamido)(6,6-dimethylcyclohexadienyl)dimethylsilanetitaniumdimethyl,  
 10 (tert-butylamido)(1,1-dimethyl-2,3,4,9,10- $\eta$ -1,4,5,6,7,8-hexahydronaphthalen-4-  
 yl)dimethylsilanetitaniumdimethyl,  
 (tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10- $\eta$ -1,4,5,6,7,8-hexahydronaphthalen-4-  
 yl)dimethylsilanetitaniumdimethyl  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl methylphenylsilanetitanium (IV)  
 15 dimethyl,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl methylphenylsilanetitanium (II)  
 1,4-diphenyl-1,3-butadiene,  
 1-(tert-butylamido)-2-(tetramethyl- $\eta^5$ -cyclopentadienyl)ethanediyltitanium (IV)  
 dimethyl, and  
 20 1-(tert-butylamido)-2-(tetramethyl- $\eta^5$ -cyclopentadienyl)ethanediyl- titanium (II) 1,4-  
 diphenyl-1,3-butadiene.

Complexes containing two K' groups including bridged complexes suitable for use in the present invention include:

- bis(cyclopentadienyl)zirconiumdimethyl,  
 25 bis(cyclopentadienyl)zirconium dibenzyl,  
 bis(cyclopentadienyl)zirconium methyl benzyl,  
 bis(cyclopentadienyl)zirconium methyl phenyl,  
 bis(cyclopentadienyl)zirconiumdiphenyl,  
 bis(cyclopentadienyl)titanium-allyl,  
 30 bis(cyclopentadienyl)zirconiummethylmethoxide,  
 bis(cyclopentadienyl)zirconiummethylchloride,

- bis(pentamethylcyclopentadienyl)zirconiumdimethyl,  
bis(pentamethylcyclopentadienyl)titaniumdimethyl,  
bis(indenyl)zirconiumdimethyl,  
indenylfluorenylzirconiumdimethyl,  
5 bis(indenyl)zirconiummethyl(2-(dimethylamino)benzyl),  
bis(indenyl)zirconiummethyltrimethylsilyl,  
bis(tetrahydroindenyl)zirconiummethyltrimethylsilyl,  
bis(pentamethylcyclopentadienyl)zirconiummethylbenzyl,  
bis(pentamethylcyclopentadienyl)zirconiumdibenzyl,  
10 bis(pentamethylcyclopentadienyl)zirconiummethoxymethoxide,  
bis(pentamethylcyclopentadienyl)zirconiummethylchloride,  
bis(methylethylcyclopentadienyl)zirconiumdimethyl,  
bis(butylcyclopentadienyl)zirconiumdibenzyl,  
bis(t-butylcyclopentadienyl)zirconiumdimethyl,  
15 bis(ethyltetramethylcyclopentadienyl)zirconiumdimethyl,  
bis(methylpropylcyclopentadienyl)zirconiumdibenzyl,  
bis(trimethylsilylcyclopentadienyl)zirconiumdibenzyl,  
dimethylsilyl-bis(cyclopentadienyl)zirconiumdimethyl,  
dimethylsilyl-bis(tetramethylcyclopentadienyl)titanium (III) allyl  
20 dimethylsilyl-bis(t-butylcyclopentadienyl)zirconiumdichloride,  
dimethylsilyl-bis(n-butylcyclopentadienyl)zirconiumdichloride,  
(methylene-bis(tetramethylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,  
(methylene-bis(n-butylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,  
dimethylsilyl-bis(indenyl)zirconiumbenzylchloride,  
25 dimethylsilyl-bis(2-methylindenyl)zirconiumdimethyl,  
dimethylsilyl-bis(2-methyl-4-phenylindenyl)zirconiumdimethyl,  
dimethylsilyl-bis(2-methylindenyl)zirconium-1,4-diphenyl-1,3-butadiene,  
dimethylsilyl-bis(2-methyl-4-phenylindenyl)zirconium (II) 1,4-diphenyl-1,3-butadiene,  
dimethylsilyl-bis(tetrahydroindenyl)zirconium(II) 1,4-diphenyl-1,3-butadiene,  
30 dimethylsilyl-bis(fluorenyl)zirconiummethylchloride,  
dimethylsilyl-bis(tetrahydrofluorenyl)zirconium bis(trimethylsilyl),

(isopropylidene)(cyclopentadienyl)(fluorenyl)zirconiumdibenzyl, and dimethylsilyl(tetramethylcyclopentadienyl)(fluorenyl)zirconium dimethyl.

Other acid activated polymerization catalysts (including Ziegler-Natta catalysts and Brookhart/Gibson catalysts) will, of course, be apparent to those skilled in the art and are to be included within the scope of the instant invention as if they were a metallocene polymerization catalyst. The metallocene polymerization catalyst can alternatively be added during the dispersion of the layered silicate material. The relative amount of metallocene polymerization catalyst is the same in the instant invention as in the prior art of metallocene catalysts and depends on the specific catalyst used. It should be understood that the instant invention may be used for any polymerization process including solution, slurry and gas phase polymerization and that any polymerization catalyst may be used that is acid activated.

When an olefin is added to the metallocene polymerization catalyst treated dispersion of the acid treated cation exchanging layered silicate material, the olefin polymerizes to form the nanocomposite polymer. It is believed that the acid component of the acidified layered silicate material activates the metallocene polymerization catalyst to produce polymer between the layers of the layered silicate material and thereby separate or exfoliate such layers to a greater degree into the developing polymer matrix. In addition, it is believed that the temperature of the polymerization should be sufficiently low so that more of the polymerization occurs between the layers of the layered silicate in order to promote a greater degree of such exfoliation.

Preferably, before contacting the dispersion with the metallocene polymerization catalyst, the residual hydroxyl or other reactive functionality of the acid treated cation exchanging layered silicate material is capped or reacted with a reactive material, especially a Lewis acid. Preferred Lewis acids include trialkyl aluminum compounds having from 1 to 10 carbons in each alkyl group.

The term "metallocene polymerization catalyst treated, acid treated cation exchanging layered silicate material" means a cation exchanging layered silicate material that has been contacted with an acid and a metallocene polymerization catalyst as discussed above. It should be understood that a metallocene polymerization catalyst treated, acid



treated cation exchanging layered silicate material may be used in a solution, slurry or gas phase polymerization system.

The resulting nanocomposite polymer preferably comprises an exfoliated acid treated cation exchanging layered silicate material dispersed in a polymer matrix,  
5 wherein more than about fifty percent by weight of the acid treated layered silicate material is found by electron microscopy of the nanocomposite polymer to have five or fewer layers.

Preferably, the weight percent of acid treated cation exchanging layered silicate material in the nanocomposite polymer is more than one percent and less than ten percent. Such nanocomposite polymers are capable of unexpected tensile modulus, such as,  
10 more than four hundred thousand pounds per square inch. With specific regard to polypropylene nanocomposites, unexpected tensile modulus of more than five hundred thousand pounds per square inch are described below. The standard test method for determining tensile modulus herein is ASTM Method Number D882.

Preferably, the olefin used in the instant invention is selected from the group  
15 of olefins having from two to ten carbon atoms. Such olefins include, for example, styrene, divinylbenzene, norbornene, ethylene, propylene, octene, butadiene and mixtures thereof. Thus, the polymer product of or by way of the instant invention may be, for example, a rubber, a thermoplastic elastomer, polyethylene and polypropylene.

## 20 EXAMPLE 1

One half gram of vacuum dried 4-tetradecylanilinium exchanged montmorillonite is added to one hundred and twenty milliliters of dry toluene to produce a slurry. Six hundred microliters of tripropylaluminum is added to the slurry. Five hundred microliters of a two and one half millimolar solution of metallocene polymerization catalyst  
25 (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for fifteen minutes. The sonicated slurry is then aged for one hour. Then, propylene gas at ten pounds per square inch is contacted with the slurry for fifty minutes at room temperature. Seven grams of polypropylene nanocomposite is recovered by acetone precipitation. The polymer has a number average  
30 molecular weight of 98,900. Electron microscopy of the polymer shows substantial single layer exfoliation of the montmorillonite.

**EXAMPLE 2**

Example 1 is repeated except that the polymerization reaction is one half hour at room temperature followed by one half hour at eighty degrees Celcius. Seven grams  
5 of polypropylene nanocomposite is recovered by acetone precipitation. The polymer has a number average molecular weight of 17,100. Electron microscopy of the polymer shows substantial single layer exfoliation of the montmorillonite but to a somewhat lesser degree than the polymer of Example 1.

10 **EXAMPLE 3**

Example 1 is repeated except that one-quarter gram of treated montmorillonite is used and the polymerization reaction is one hour at eighty degrees Celcius. Seven grams of polypropylene nanocomposite is recovered by acetone precipitation. The polymer has a number average molecular weight of 6,200. Electron  
15 microscopy of the polymer shows substantial single layer exfoliation of the montmorillonite but to a somewhat lesser degree than the polymer of Example 2.

**EXAMPLE 4**

Example 1 is repeated except that one-quarter gram of treated montmorillonite is used and the polymerization reaction is three quarters of one hour at  
20 room temperature. Seven grams of polypropylene nanocomposite is recovered by acetone precipitation. The polymer has a number average molecular weight of 103,000. Electron microscopy of the polymer shows substantial single layer exfoliation of the montmorillonite to about the same degree than the polymer of Example 1.

25

**EXAMPLE 5**

Example 1 is repeated except that one-quarter gram of treated montmorillonite is used and the polymerization reaction is one quarter of one hour at eighty-five degrees Celcius. Ten grams of polypropylene nanocomposite is recovered by acetone

precipitation. The polymer has a number average molecular weight of 18,700. Electron microscopy of the polymer shows some single layer exfoliation of the montmorillonite but less than that of Example 3.

5    **EXAMPLE 6**

Two grams of vacuum dried 4-tetradecylanilinium exchanged montmorillonite is added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of tripropylaluminum is added to the slurry. Five hundred microliters of a two and one half millimolar solution of metallocene polymerization catalyst (dimethylsilyl-  
10    bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for thirty minutes. The sonicated slurry is then aged for sixteen hours. Then, propylene gas at twenty pounds per square inch is contacted with the slurry for thirty minutes at room temperature. Thirty grams of the resulting polypropylene nanocomposite is recovered. The tensile modulus of the resulting polypropylene  
15    nanocomposite is five hundred and one thousand pounds per square inch. Electron microscopy examination of the resulting polypropylene nanocomposite shows substantial single layer exfoliation of the montmorillonite.

**EXAMPLE 7**

20            Example 6 is repeated except that the polymerization reaction is carried out for fifteen minutes. Fifteen grams of the resulting polypropylene nanocomposite is recovered. The tensile modulus of the resulting polypropylene nanocomposite is four hundred and eighty three thousand pounds per square inch. Electron microscopy examination of the resulting polypropylene nanocomposite shows substantial single layer  
25    exfoliation of the montmorillonite but to a somewhat lesser degree than that of Example 6.

**EXAMPLE 8**

Two grams of vacuum dried 4-tetradecylanilinium exchanged fluoromica is added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of one  
30    molar tripropylaluminum in toluene is added to the slurry. One milliliter of a one and one

quarter millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for thirty minutes. The sonicated slurry is then aged for five hours. Then, propylene gas at twenty pounds per square inch is contacted with the slurry for fifteen minutes at room temperature. Twelve grams of polypropylene nanocomposite is recovered by acetone precipitation. The polymer has a number average molecular weight of 169,000. The tensile modulus of the polypropylene nanocomposite is 695,000 pounds per square inch (psi).

#### 10 EXAMPLE 9

Two grams of vacuum dried 4-tetradecylanilinium exchanged fluoromica is added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of one molar tripropylaluminum in toluene is added to the slurry. One milliliter of a one and one quarter millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for thirty minutes. The sonicated slurry is then aged for one day. Then, propylene gas at twenty pounds per square inch is contacted with the slurry for thirty minutes at room temperature. Twenty five grams of polypropylene nanocomposite is recovered by acetone precipitation. The polymer has a number average molecular weight of 170,000. The tensile modulus of the polypropylene nanocomposite is 434,000 pounds per square inch (psi).

#### EXAMPLE 10

The experiment of Example 9 is repeated six times using the polymerization times noted below.

<u>Pol. Time</u>	<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
30 minutes	143,000	401,000 psi	23 grams
20 minutes	246,000	456,000 psi	16 grams
20 minutes	228,000	461,000 psi	18 grams
60 minutes	not det.	413,000 psi	30 grams
10 minutes	191,000	457,000 psi	12 grams
10 minutes	191,000	457,000 psi	12 grams

#### EXAMPLE 11

Two grams of vacuum dried 4-tetradecylanilinium exchanged montmorillonite is  
5 added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of one  
molar tripropylaluminum in toluene is added to the slurry. One milliliter of a one and one  
quarter millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-  
methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry.  
The slurry is then sonicated for twenty minutes. The sonicated slurry is then aged for one  
10 hour. Then, propylene gas at twenty pounds per square inch is contacted with the slurry for  
thirty minutes at room temperature. Twenty grams of polypropylene nanocomposite is  
recovered by acetone precipitation. The polymer has a number average molecular weight of  
303,000. The tensile modulus of the polypropylene nanocomposite is 522,000 pounds per  
square inch (psi).

15

#### EXAMPLE 12

The experiment of Example 11 is repeated five times with the following results.

<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
200,000	578,000 psi	22 grams
229,000	590,000 psi	19 grams
245,000	548,000 psi	21 grams
205,000	413,000 psi	21 grams
191,000	427,000 psi	21 grams

## EXAMPLE 13

Two grams of vacuum dried anilinium exchanged montmorillonite is added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of one molar tripropylaluminum in toluene is added to the slurry. Two milliliters of a one and one quarter millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for thirty minutes. The sonicated slurry is then aged for one hour. Then, propylene gas at twenty pounds per square inch is contacted with the slurry at the temperatures shown below with the following results.

<u>Pol. Temp.</u>	<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
22 deg. C	213,000	427,000 psi	12 grams
22 deg. C	260,000	402,000 psi	14 grams
40 deg. C	133, 000	656,000 psi	14 grams
50 deg. C	149,000	641,000 psi	17 grams
50 deg. C.	125,000	586,000 psi	20 grams
50 deg. C	165,000	596,000 psi	22 grams
50 deg. C	176,000	563,000 psi	22 grams
50 deg. C	184,000	412,000 psi	18 grams
50 deg. C	114,000	441,000 psi	17 grams

## EXAMPLE 14

One gram of vacuum dried anilinium exchanged montmorillonite is added to one hundred milliliters of dry toluene to produce a slurry. Five milliliters of one molar tripropylaluminum in toluene is added to the slurry. One milliliter of a one and one quarter millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for thirty minutes. The sonicated slurry is then aged for one hour. Then, propylene gas at twenty pounds per square inch is contacted with the slurry at the temperatures shown below with the following results.

<u>Pol. Temp.</u>	<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
55 deg. C	not det.	419,000 psi	10 grams
50 deg. C	134,000	429,000 psi	11 grams
50 deg. C	134,000	429,000 psi	11 grams

10

## EXAMPLE 15

One gram of vacuum dried anilinium exchanged montmorillonite is added to one hundred milliliters of dry toluene to produce a slurry. Five milliliters of one molar tripropylaluminum in toluene is added to the slurry. Two milliliters of a one and one quarter millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for thirty minutes. The sonicated slurry is then aged for one hour. Then, propylene gas at twenty pounds per square inch is contacted with the slurry at the temperatures shown below with the following results.

<u>Pol. Temp.</u>	<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
55 deg. C	125,000	402,000 psi	32 grams
22 deg. C	207,000	411,000 psi	14 grams
22 deg. C	195,000	457,000 psi	12 grams
60 deg. C	94,000	447,000 psi	10 grams

## EXAMPLE 16

Two grams of freeze dried hydrochloric acid treated attapulgite is added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of one molar tripropylaluminum in toluene is added to the slurry. One milliliter of a one and one quarter  
 5 millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for thirty minutes. The sonicated slurry is then aged for one hour. Then, propylene gas at twenty pounds per square inch is contacted with the slurry at the temperatures shown below with the following results.

<u>Pol. Temp.</u>	<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
22 deg. C	235,000	461,000 psi	14 grams
22 deg. C	245,000	461,000 psi	14 grams
22 deg. C	251,000	446,000 psi	14 grams
22 deg. C	212,000	443,000 psi	15 grams
22 deg. C	307,000	453,000 psi	19 grams
22 deg. C	264,000	443,000 psi	18 grams
22 deg. C	256,000	436,000 psi	19 grams
50 deg. C	153,000	743,000 psi	18 grams
50 deg. C	181,000	761,000 psi	18 grams
50 deg. C	178,000	779,000 psi	15 grams

10

## EXAMPLE 17

One gram of freeze dried hydrochloric acid treated attapulgite is added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of one molar tripropylaluminum in toluene is added to the slurry. One milliliter of a one and one quarter  
 15 millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry is then sonicated for thirty minutes. The sonicated slurry is then aged for one hour. Then,



propylene gas at twenty pounds per square inch is contacted with the slurry at the temperatures shown below with the following results.

<u>Pol. Temp.</u>	<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
50 deg. C	154,000	606,000 psi	13 grams
50 deg. C	154,000	433,000 psi	14 grams
50 deg. C	186,000	427,000 psi	12 grams

#### EXAMPLE 18

5 One gram of freeze dried hydrochloric acid treated attapulgite is added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of one molar tripropylaluminum in toluene is added to the slurry. Two milliliters of a one and one quarter millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry  
10 is then sonicated for thirty minutes. The sonicated slurry is then aged for one hour. Then, propylene gas at twenty pounds per square inch is contacted with the slurry at the temperatures shown below with the following results.

<u>Pol. Temp.</u>	<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
50 deg. C	138,000	408,000 psi	14 grams
50 deg. C	133,000	407,000 psi	13 grams
50 deg. C	138,000	416,000 psi	14 grams
50 deg. C	134,000	421,000 psi	13 grams

#### EXAMPLE 19

15 Two grams of tetradecylaluminum treated fluoromica is added to four hundred milliliters of dry toluene to produce a slurry. Five milliliters of one molar tripropylaluminum in toluene is added to the slurry. One milliliter of a one and one quarter millimolar solution of metallocene polymerization catalyst (dimethylsilyl-bis(2-methyl-4-phenylindenyls) zirconium (II) 1,4-diphenyl-1,3-butadiene) is added to the slurry. The slurry

is then sonicated for thirty minutes. The sonicated slurry is then aged for one day. Then, ethylene gas at ten pounds per square inch is contacted with the slurry at the temperatures shown below with the following results.

<u>Pol. Temp.</u>	<u>Molecular Wt.</u>	<u>Tensile Mod.</u>	<u>Pol. Wt.</u>
70 deg. C	115,000	400,000 psi	11 grams
70 deg. C	115,000	400,000 psi	12 grams
22 deg. C	327,000	not determined	6 grams
70 deg. C	not det.	389,000 psi	11 grams
70 deg. C	not det.	389,000 psi	11 grams

WHAT IS CLAIMED IS:

1. A method for producing a nanocomposite polymer, comprising the step of: adding an olefin to a metallocene polymerization catalyst treated dispersion of an acid  
5 treated cation exchanging layered silicate material in a solvent so that the olefin polymerizes to form the nanocomposite polymer.
2. The method of Claim 1, wherein the acid treated cation exchanging layered silicate material is acid treated with an acidified amine.
3. The method of Claim 1, wherein the acid treated cation exchanging  
10 layered silicate material is acid treated with an amine hydrochloride.
4. The method of Claim 3, wherein the amine hydrochloride is 4-tetradecyl aniline hydrochloride.
5. The method of Claim 1 wherein the acid treated cation exchanging layered silicate material is acidified with an inorganic Bronsted acid.
- 15 6. The method of Claim 1, wherein the acid treated layered silicate material has been contacted with a capping agent.
7. The method of Claim 6, wherein the capping agent is a trialkyl aluminum compound.
8. The method of Claim 7, wherein the trialkyl aluminum compound is  
20 tripropyl aluminum.
9. The method of Claim 1, wherein more than about fifty percent by weight of the acid treated layered silicate material is found by electron microscopy of the nanocomposite polymer to have five or fewer layers.
10. The method of Claim 9, wherein in step (c) the olefin is selected from  
25 the group consisting of olefins having from two to ten carbon atoms and mixtures thereof.
11. The method of Claim 10, wherein the olefin comprises an olefin selected from the group consisting of styrene and divinylbenzene.
12. The method of Claim 10, wherein the olefin comprises norbornene.
13. The method of Claim 10, wherein the olefin comprises ethylene.

14. The method of Claim 10, wherein the olefin comprises propylene.
15. The method of Claim 1, wherein the cation exchanging layered silicate material is selected from the group consisting of montmorillonite, hectorite, mica, saponite, fluorohectorite, fluoromica, sepiolite, attapulgite, and a layered zeolite.
- 5           16. A composition of matter, comprising an exfoliated acid treated cation exchanging layered silicate material dispersed in a polymer matrix, wherein more than about fifty percent of the acid treated cation exchanging layered silicate material is found by electron microscopy to have five or fewer layers.
- 10           17. The composition of Claim 16, wherein the cation exchanging layered silicate material is selected from the group consisting of montmorillonite, hectorite, mica, saponite, fluorohectorite, fluoromica, sepiolite, attapulgite, and a layered zeolite, which material has been contacted with an acid.
18. The composition of Claim 16, wherein the acid is an acidified amine.
19. The composition of Claim 16, wherein the acid is an inorganic Bronsted  
15   acid.
20. The composition of Claim 18, wherein the amine hydrochloride is 4-tetradecylalanine hydrochloride.
21. The composition of Claim 16, wherein the polymer comprises polymerized olefin monomer.
- 20           22. The composition of Claim 21, wherein the olefin monomer is selected from the group consisting of olefins having from two to ten carbon atoms and mixtures thereof.
23. The composition of Claim 21 wherein the olefin monomer comprises ethylene.
- 25           24. The composition of Claim 21 wherein the olefin monomer comprises propylene.
25. The composition of Claim 21, wherein the amount of acid treated cation exchanging layered silicate is less than ten weight percent of the nanocomposite polymer

and the tensile modulus of the nanocomposite polymer is greater than 350,000 pounds per square inch.

26. The composition of Claim 21, wherein the amount of acid treated cation exchanging layered silicate is ten weight percent or less of the nanocomposite polymer and the tensile modulus of the nanocomposite polymer is greater than 400,000 pounds per square inch.

27. The composition of Claim 21, wherein the amount of acid treated cation exchanging layered silicate is ten weight percent or less of the nanocomposite polymer and the tensile modulus of the nanocomposite polymer is greater than 500,000 pounds per square inch.

28. The composition of Claim 21, wherein the amount of acid treated cation exchanging layered silicate is ten weight percent or less of the nanocomposite polymer and the tensile modulus of the nanocomposite polymer is greater than 600,000 pounds per square inch.

29. The composition of Claim 21, wherein the olefin monomer is selected from the group consisting of norbornene, styrene, divinyl benzene, butadiene and mixtures thereof.

30. A composition of matter, comprising: a metallocene polymerization catalyst treated, acid treated cation exchanging layered silicate material.

31. The composition of Claim 30, wherein the cation exchanging layered silicate material is selected from the group consisting of montmorillonite, hectorite, mica, saponite, fluorohectorite, fluoromica, sepiolite, attapulgite, and a layered zeolite, which material has been contacted with an acid.

32. The composition of Claim 30, wherein the acid is an acidified amine.

33. The composition of Claim 30, wherein the acid is an inorganic Bronsted acid.

34. The composition of Claim 32, wherein the amine hydrochloride is 4-tetradecylalanine hydrochloride.

35. The composition of Claim 30, wherein the polymer comprises polymerized olefin monomer.

36. The composition of Claim 35, wherein the olefin monomer is selected from the group consisting of olefins having from two to ten carbon atoms and mixtures thereof.

37. The composition of Claim 35 wherein the olefin monomer comprises ethylene.

38. The composition of Claim 35 wherein the olefin monomer comprises propylene.

39. The composition of Claim 38, wherein the amount of acid treated cation exchanging layered silicate is ten weight percent or less of the nanocomposite polymer and the tensile modulus of the nanocomposite polymer is greater than 350,000 pounds per square inch.

40. The composition of Claim 38, wherein the amount of acid treated cation exchanging layered silicate is ten weight percent or less of the nanocomposite polymer and the tensile modulus of the nanocomposite polymer is greater than 400,000 pounds per square inch.

41. The composition of Claim 38, wherein the amount of acid treated cation exchanging layered silicate is ten weight percent or less of the nanocomposite polymer and the tensile modulus of the nanocomposite polymer is greater than 500,000 pounds per square inch.

42. The composition of Claim 38, wherein the amount of acid treated cation exchanging layered silicate is ten weight percent or less of the nanocomposite polymer and the tensile modulus of the nanocomposite polymer is greater than 600,000 pounds per square inch.

43. The composition of Claim 35, wherein the olefin monomer is selected from the group consisting of norborene, styrene, divinyl benzene, butadiene and mixtures thereof.

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